Cordylite-(Ce): A crystal chemical investigation of material from four localities, including type material

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ABSTRACT

Six cordylites from the four known localities (Narssarssuk (Greenland), Mont St. Hilaire (Canada), Bayan Obo (China), and Kola Peninsula (Russia)) were investigated by electron microprobe and X-ray single-crystal structure determination, and a seventh sample was investigated by X-ray methods only. The material studied included type cordylite. The idealized formula for cordylite is redefined as (Na, Ca, Ba)Ce(CO,)₈, 0 < x < 1, with Ce for the sum of REE; the SrO content may reach about 5.7 wt%. All of our structure refinements (P6₃/mmc; a = 5.10, c = 23.10 Å) agree very well among themselves and with the published structures of “baiyuneboite-(Ce)” and unnamed (Ca, Ba)Ce(CO,)₈F. Cordylite has a sheet structure formed of (001) layers of [Ba][CO₃][Ce,CO₃][Na,F][Ce,CO₃][CO₃][Ba] stacked along [001]. The interatomic distances are as expected, with the exception of unshielded Na-F distances of 2.94 Å; unlike the carbonate groups in basnlisite and synchysite, the carbonate groups in cordylite-(Ce) are parallel (001). Investigation of type cordylite showed that the formula proposed by Flink, i.e., BaCe₆(CO₃)₂F₂, is to be modified to that given above, with x = 0 for Flink’s material. Baiyuneboite-(Ce), a mineral previously approved by the IMA CNMMN but later withdrawn because of potential similarities with cordylite, is confirmed here as being essentially identical to type cordylite.

INTRODUCTION

Cordylite-(RE) is a member of the rare earth (RE) fluorocarbonate minerals, a group of minerals that supplies the vast majority of the world’s supply of RE elements. The name cordylite was introduced by Flink (1899) for a rare mineral in an alkali pegmatite from Narssarssuk, Greenland. From wax-yellow crystals up to 3 mm in size, Flink determined hexagonal symmetry on the basis of morphology. Chemical analysis led to the formula Ce,F,BaC₈, with the remark that the data did not exactly match the formula. Flink emphasized the close similarity in chemical composition between cordylite and parisite, with Ba in cordylite corresponding to Ca in parisite. Böggild (1906) added to the morphological knowledge and determined refractive indices. Ofstedal (1931) added oscillation photographs to derive a hexagonal cell with a = 4.35, c = 22.8 Å, and a space group with highest possible symmetry P6₃/mmc. He postulated cell contents of Ba,Ce,F₆(CO₃)₈, and determined the coordinates of the Ba and Ce atoms. Ofstedal (1931) mistakenly published d₀₀₀ for a. His value for a should have been 5.02 Å, in good agreement with modern values. This change gives reasonable agreement of d₀₀₀ with dₓₓₓ and is consistent with subsequent measurements by Donnay and Donnay (1955). Donnay and Donnay (1955) considered the space group to be P6₂c or P6₃/mmc. On the basis of strong negative birefringence they postulated that the planes of the carbonate groups were oriented perpendicular to the c axis.

Chen and Chao’s (1975) measurements of two tiny crystals from pegmatite dike of the nepheline syenite of Mont St. Hilaire, Quebec, Canada, confirmed the X-ray results of Donnay and Donnay (1955). On the basis of an electron microprobe analysis, the formula is (Ba₀.₉₂Ca₀.₀₇Sr₀.₀₄)(Ce₁.₇La₀₉Th₀.₀₁)(CO₃)₁₀F₁.₅. The deficiency of F was attributed to the omission of H₂O during the analysis. No Na was reported. However, this element was found in re-examination of the data (letters of G.Y. Chao to J. Zemann).

Discovery of similar material in the enormous REE deposit at Bayan Obo, Inner Mongolia, China, complicated matters. Zhang and Tao (1985) considered the material as cordylite, but drew attention to a Na₂O content of 1.79 wt%. Fu and Su (1987) named a mineral from the same locality “baiyuneboite-(Ce).” Its X-ray crystallographic and optical constants were very close to those published previously for cordylite (Donnay and Donnay
1955; Chen and Chao 1975). On the basis of 10 micro-
probe analyses [with Na, O = 4.7(4) wt% and F = 2.5(2) wt%] and in agreement with a careful X-ray structure deter-
dination in space group P6./mnc. Fu et al. (1987) derived the idealized formula NaBaCe(CO,).F. The name was approved by CNMMN of the IMA, but approval was late-
ly withdrawn by the Chairman of the Commission be-
cause bayuneboite and cordylite could be identical (Jamb-
or and Grew 1990).

Shen and Mi (1991) published the determination of an
unnamed mineral from Bayan Obo with the ideal formula
(Cao,□,□)BaCe(CO,).F. The lattice constants were very
close to those published for cordylite (Donnay and Don-
nay 1955; Chen and Chao 1975) and for bayuneboite (Fu
et al. 1987), but in the structure determination they used
space group P62c, a subgroup of P6/mmc. Their atomic
arrangement is very close to that published by Fu et al.
(1987) for bayuneboite, but with 0.5 Ca instead of 1.0
Na. Shen and Mi (1992) later concluded that the previous
formula of cordylite (Flink 1989), as well as the deduced
structure (Oftedal 1931), had to be incorrect and that the
real formula of cordylite should be (Na,_,Ca„r)
BaCe(CO,).F. Zaitsev et al. (1990) analyzed cordylite
from the carbonatites of the Kola Peninsula, Russia, and
found relatively high contents of SrO and FeO but re-
tained the formula BaCe(CO,).F for the mineral.

For general information on the mineralogy, the reader
is referred to Böggild (1953) for Narsarsuk, to Horvath
and Gaul (1990) for Mont St. Hilaire, and to Zhang and
Tao (1986) and Zhang et al. (1995) for Bayan Obo.

The aim of this work is to clarify the relationships
among the various phases reported as cordylite (or kor-
dylite) (including cordylite-(Ce), “bayuneboite-(Ce),”
and unnamed (Ca„r□,□)BaCe(CO,).F) and the phase from
the different localities, and to clarify the no-
mencature problems of this mineral. Two groups were
working on the problem simultaneously, and we have
combined our several crystal structure and chemical
analyses. Thus portions of the work listed below are attributed
to the “Miami group” or the “Vienna group.” Although
affiliations are listed above, the Vienna Group also in-
cludes Yang Zhuming, Beijing, who did crystal structure
work in Vienna on material from Bayan Obo and from
the Kola Peninsula, and J.J. Rønsbo, Copenhagen, who
did microprobe work on type cordylite from Greenland
and on cordylite from Mont St. Hilaire, both structurally
investigated in Vienna. We demonstrate that the earlier
proposed mineral “bayuneboite” or “bayuneboite-
(Ce)” is actually cordylite-(Ce), validating the withdraw-
al of mineral status by the IMA CNMMN. In this work,
Ce always stands for the sum of rare earth elements.

**Experimental methods**

The Miami group refined the atomic arrangement of
two cordylite-(Ce) samples. One is from an alkaline peg-
mattie, Narsarsuk, Greenland (Harvard Mineralogical
Museum no. 84438), where the type sample of cordylite-
(Ce) was found by Flink (1899). It is transparent, sub-
hedral, and slightly yellowish, coexisting with synchysite-
(Ce) and other alkaline minerals. The other is from Mont
St. Hilaire, Quebec, Canada. It is an euhedral, optical-
quality hexagonal plate, slightly yellowish in color. Good
(001) cleavage can be found in both the samples.

The Vienna group investigated cordylite-(Ce) from all
four known localities. The cordylite from Narsarsuk
was type material from the mineral collection of the Geo-
logisk Museum, Copenhagen. From the same collection
an original crystal of Flink (1899), M.M. no. 392, was
investigated by single-crystal X-ray diffractometry. A
standard microprobe analysis of this crystal (designated
“Narsarsuk 1”) in Tables 1–5) could not be obtained
because the beam seriously damaged the crystal. A qual-
itative EDX test showed, however, appreciable amounts
of Na, contrary to the analysis published by Flink (1899).

In both groups the crystals were carefully checked by
photographic X-ray methods before intensity collection.

The structure investigations were made in Vienna on a
STOE AED2 diffractometer using program system
SHELXL-93 (Sheldrick 1993), with absorption correction
by Ψ scans. The Miami investigations were undertaken
on an Enraf-Nonius CAD-4 diffractometer using the SDP
package of programs (Frenz 1985), with absorption cor-
rections by Ψ scans and subsequently by the absorption
surface method as implemented in program DIFABS
(Walker and Stuart 1983). Both groups used graphite
monochromated Mo-radiation. In Vienna, unit-cell pa-
rameters constrained to hexagonal symmetry were ob-
tained for the five cordylites by least-squares methods
from carefully measured setting angles of 24 to 48 re-
flections; at Miami, unconstrained unit-cell parameters
were obtained in both cases by the same procedure from
25 setting angles. Further details of data collection and
crystal data are contained in Table 1; for complete details
of the Miami experimental procedures, the reader is re-
ferred to Ni et al. (1993).

The solution of the structures was not difficult, either
by Patterson and subsequent Fourier methods or by direct
methods (Multan-80; Main et al. 1980). The ideal formula
obtained for all crystals is (Na,_,Ca„r)BaCe(CO,).F. 0
\( < x < 1 \) ; the value of x could not be determined by X-
ray methods because the scattering power of Ca is close
to twice that of Na. All crystals contain some Sr (Table
5) but the content never exceeds a few weight percent.
The final least-squares refinements were made in space
group P6/mmc. Refinements were also attempted in the
subgroup P62c but no conclusive indications to prefer this
space group were found.

The atomic coordinates obtained are compiled in Table
2, the anisotropic displacement parameters in Table 3.
TABLE 1. Crystal data and technical details on structure refinement for cordylite from various localities

<table>
<thead>
<tr>
<th>Locality</th>
<th>Narssarssuk</th>
<th>Mont St. Hilaire</th>
<th>Kola Pen.</th>
<th>Bayan Obo</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.0905(8)</td>
<td>5.1011(4)</td>
<td>5.0913(7)</td>
<td>5.108(1)</td>
</tr>
<tr>
<td>b</td>
<td>5.0905(8)</td>
<td>5.1011(4)</td>
<td>5.0913(7)</td>
<td>5.108(1)</td>
</tr>
<tr>
<td>c</td>
<td>23.102(10)</td>
<td>23.096(4)</td>
<td>23.070(5)</td>
<td>23.129(10)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
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<td>β</td>
<td>90</td>
<td>90</td>
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<td>90</td>
</tr>
<tr>
<td>γ</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>518.4(5)</td>
<td>520.5(2)</td>
<td>517.9(3)</td>
<td>522.6(2)</td>
</tr>
<tr>
<td>2ω max (°)</td>
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<td>70</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>No. data pts.</td>
<td>1342</td>
<td>563</td>
<td>504</td>
<td>289</td>
</tr>
<tr>
<td>No. unique</td>
<td>682</td>
<td>597</td>
<td>260</td>
<td>298</td>
</tr>
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</table>

Notes: Numbers in parentheses denote one standard deviation. 1 = Results from Vienna group, $R_{ave}$ values of Vienna group are based on $F$. 2 = Results from Miami group, $R_{ave}$ values of the Miami group are based on $F$. 3 = Type sample from Narssarssuk, Greenland. 4 = For refinements of Vienna group:

- $R = \sum |F_o| - |F_c|/\sum |F_o|$
- $R_\alpha = \sum F_o^2 - F_c^2)/\sum F_o^2$;
- $w = \sum (1/(\sigma^2(F_c) + (a \times P^2 + b \times P))$; $P = \max (0 \text{ or } F_c^2)$ + $2F_c^2/3$.

TABLE 2. Atomic coordinates and equivalent isotropic $U(\text{Å}^2)$ for atoms in cordylite from various localities

<table>
<thead>
<tr>
<th>Locality</th>
<th>Narssarssuk</th>
<th>Mont St. Hilaire</th>
<th>Kola Pen.</th>
<th>Bayan Obo</th>
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<tr>
<td>x</td>
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<td>0</td>
<td>0</td>
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<td>y</td>
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<td>z</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Ce</td>
<td>0.019(4)</td>
<td>0.02(6)</td>
<td>0.016(5)</td>
<td>0.0124(5)</td>
</tr>
<tr>
<td>x</td>
<td>1/3</td>
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<td>1/3</td>
<td>1/3</td>
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<td>y</td>
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<td>2/3</td>
<td>2/3</td>
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<td>3/4</td>
<td>3/4</td>
<td>3/4</td>
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<tr>
<td>Na</td>
<td>0.007(1)</td>
<td>0.016(1)</td>
<td>0.02(2)</td>
<td>0.02(2)</td>
</tr>
<tr>
<td>x</td>
<td>1/3</td>
<td>1/3</td>
<td>1/3</td>
<td>1/3</td>
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<td>y</td>
<td>2/3</td>
<td>2/3</td>
<td>2/3</td>
<td>2/3</td>
</tr>
<tr>
<td>z</td>
<td>3/4</td>
<td>3/4</td>
<td>3/4</td>
<td>3/4</td>
</tr>
<tr>
<td>F</td>
<td>0.031(4)</td>
<td>0.038(2)</td>
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<td>0.034(7)</td>
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<tr>
<td>x</td>
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<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>y</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>z</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>O1</td>
<td>0.6775(4)</td>
<td>0.6780(2)</td>
<td>0.6802(5)</td>
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</tr>
<tr>
<td>x</td>
<td>0.1448(6)</td>
<td>0.1448(3)</td>
<td>0.1448(7)</td>
<td>0.1452(12)</td>
</tr>
<tr>
<td>y</td>
<td>2×</td>
<td>2×</td>
<td>2×</td>
<td>2×</td>
</tr>
<tr>
<td>z</td>
<td>0.6764(2)</td>
<td>0.6763(1)</td>
<td>0.6761(2)</td>
<td>0.6758(4)</td>
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<tr>
<td>O2</td>
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<td>0.014(1)</td>
<td>0.011(3)</td>
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<tr>
<td>x</td>
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<td>0.5218(4)</td>
<td>0.5210(8)</td>
<td>0.5197(12)</td>
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<tr>
<td>y</td>
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<td>2×</td>
<td>2×</td>
<td>2×</td>
</tr>
<tr>
<td>z</td>
<td>0.4334(4)</td>
<td>0.4333(3)</td>
<td>0.4326(5)</td>
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<td>C2</td>
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<td>0.014(2)</td>
<td>0.012(2)</td>
<td>0.012(2)</td>
</tr>
<tr>
<td>x</td>
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<td>2/3</td>
<td>2/3</td>
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<td>y</td>
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<td>1/3</td>
<td>1/3</td>
<td>1/3</td>
</tr>
<tr>
<td>z</td>
<td>0.017(1)</td>
<td>0.022(1)</td>
<td>0.019(2)</td>
<td>0.016(2)</td>
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</tbody>
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Note: 1 = Analyzed by Vienna group; 2 = Analyzed by Miami group. Numbers in parentheses denote one standard deviation.
TABLE 4. Interatomic distances (Å) in cordylite from various localities

<table>
<thead>
<tr>
<th>Locality</th>
<th>Narssarssuk</th>
<th>Mont St, Hilaire</th>
<th>Kola Pen,</th>
<th>B. Obo</th>
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<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Ba-O₂ × 12</td>
<td>2.963(3)</td>
<td>2.959(3)</td>
<td>2.961(5)</td>
<td>2.958(4)</td>
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<tr>
<td>O₂-O₂ × 6 (h₁)</td>
<td>2.232(3)</td>
<td>2.216(2)</td>
<td>2.225(3)</td>
<td>2.215(4)</td>
</tr>
<tr>
<td>O₂-O₂ × 6 (h₂)</td>
<td>2.858(3)</td>
<td>2.842(2)</td>
<td>2.868(3)</td>
<td>2.874(2)</td>
</tr>
<tr>
<td>Ba-O₂ × 6</td>
<td>3.034(7)</td>
<td>3.072(1)</td>
<td>3.019(3)</td>
<td>3.012(4)</td>
</tr>
<tr>
<td>Ce-O₁ × 6</td>
<td>2.644(3)</td>
<td>2.651(1)</td>
<td>2.643(4)</td>
<td>2.642(3)</td>
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<tr>
<td>Ce-O₁ × 3</td>
<td>2.500(4)</td>
<td>2.502(4)</td>
<td>2.504(4)</td>
<td>2.504(3)</td>
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<tr>
<td>Ce-F × 1</td>
<td>2.3915(5)</td>
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<td>2.3876(8)</td>
<td>2.382(2)</td>
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<tr>
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<td>2.211(3)</td>
<td>2.211(3)</td>
<td>2.215(4)</td>
</tr>
<tr>
<td>O₁-O₁ × 3 (h₂)</td>
<td>2.879(3)</td>
<td>2.885(2)</td>
<td>2.882(3)</td>
<td>2.882(2)</td>
</tr>
<tr>
<td>O₁-O₁ × 6</td>
<td>2.906(6)</td>
<td>2.975(5)</td>
<td>2.973(7)</td>
<td>2.975(5)</td>
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<tr>
<td>O₂-O₂ × 3 (h₃)</td>
<td>2.858(3)</td>
<td>2.884(2)</td>
<td>2.868(3)</td>
<td>2.863(2)</td>
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<td>F-O₁ × 6</td>
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<tr>
<td>Na-O₁ × 6</td>
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<td>2.383(4)</td>
<td>2.372(3)</td>
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<tr>
<td>Na-F × 3</td>
<td>2.939</td>
<td>2.945</td>
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<tr>
<td>O₁-O₁ × 6 (h₄)</td>
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<td>2.885(2)</td>
<td>2.882(3)</td>
<td>2.877(7)</td>
</tr>
<tr>
<td>O₁-O₁ × 3 (h₅)</td>
<td>3.041(7)</td>
<td>3.040(2)</td>
<td>3.040(3)</td>
<td>3.042(5)</td>
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<tr>
<td>C₁-O₁ × 3</td>
<td>1.277(2)</td>
<td>1.280(1)</td>
<td>1.279(6)</td>
<td>1.285(4)</td>
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<td>C₁-O₁ × 3 (h₆)</td>
<td>2.211(3)</td>
<td>2.216(2)</td>
<td>2.211(3)</td>
<td>2.220(7)</td>
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<tr>
<td>Δ</td>
<td>0.03(1)</td>
<td>0.04(1)</td>
<td>0.05(1)</td>
<td>0.05(1)</td>
</tr>
<tr>
<td>C₂-O₂ × 3</td>
<td>1.289(2)</td>
<td>1.289(2)</td>
<td>1.295(5)</td>
<td>1.296(4)</td>
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<tr>
<td>C₂-O₂ × 3 (h₇)</td>
<td>2.233(2)</td>
<td>2.217(2)</td>
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<td>Δ</td>
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<td>0.03(1)</td>
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<td>0.04(1)</td>
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</table>

Notes: 1 = Analyzed by Vienna group; 2 = Analyzed by Miami group; h = Interatomic distance on (001), Δ = offset of carbon from the oxygen plane in carbonate group. Numbers in parentheses denote one standard deviation.

* Type sample of cordylite from Narssarssuk, Greenland.
† Common edge between BaO₂ and CO₃.
‡ Common edge between BaO₂ and CeO₂F.
§ Common edge between two BaO₂.
∥ Common edge between CeO₂F and CO₃.
# Common edge between CeO₂F and NaO₂.

TABLE 5. Chemical analyses and calculated chemical formulas for cordylite-(Ce) from various localities

<table>
<thead>
<tr>
<th>Locality</th>
<th>Narssarssuk</th>
<th>Mont St, Hilaire</th>
<th>Kola Pen,</th>
<th>B. Obo</th>
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<tr>
<td></td>
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<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4.73(40)</td>
<td>4.1(1)</td>
<td>4.96(15)</td>
<td>4.298(2)*</td>
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<tr>
<td>CaO</td>
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<td>0.79(5)</td>
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</tr>
<tr>
<td>BaO</td>
<td>22.22(8)</td>
<td>19.80(81)</td>
<td>22.48(29)</td>
<td>19.26(106)</td>
</tr>
<tr>
<td>SrO</td>
<td>4.14(18)</td>
<td>0.96(23)</td>
<td>0.61(11)</td>
<td>0.96(22)</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>22.10(58)</td>
<td>28.06(19)</td>
<td>24.10(41)</td>
<td>28.64(69)</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>14.81(25)</td>
<td>15.06(73)</td>
<td>13.88(73)</td>
<td>12.42(48)</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>4.58(23)</td>
<td>4.20(55)</td>
<td>5.43(34)</td>
<td>5.13(48)</td>
</tr>
<tr>
<td>Pr₂O₃</td>
<td>1.78(18)</td>
<td>2.80(52)</td>
<td>2.24(40)</td>
<td>3.20(98)</td>
</tr>
<tr>
<td>F</td>
<td>3.60(15)</td>
<td>2.45(7)</td>
<td>3.62(21)</td>
<td>3.02(47)</td>
</tr>
<tr>
<td>CO₃</td>
<td>25.36</td>
<td>21.91</td>
<td>23.40</td>
<td>22.85</td>
</tr>
<tr>
<td>Other</td>
<td>0.82</td>
<td>0.74</td>
<td>0.74</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Atoms in unit cell (Formula basis: Sr + Ba + ΣREE = 6.00)

| Na  | 2.17 | 2.23 | 2.19 | 0.57 | 0.88 | 2.00 |
| Ca  | 0.28 | 0.20 | 0.17 | 0.93 | 0.64 | 1.00 |
| Ba  | 2.06 | 2.04 | 1.73 | 2.06 | 2.15 | 2.00 |
| Sr  | 0.20 | 0.08 | 0.13 | 0.75 | 0.15 | 0.40 |
| Ce  | 1.92 | 2.05 | 2.40 | 1.65 | 2.05 | 4.00 |
| La  | 1.28 | 1.90 | 1.05 | 0.71 | 0.93 | 0.40 |
| Nd  | 0.39 | 0.45 | 0.42 | 0.63 | 0.53 | 0.20 |
| Pr  | 0.15 | 0.19 | 0.27 | 0.19 | 0.19 | 0.20 |
| F   | 2.70 | 2.66 | 2.19 | 2.00 | 2.00 | 8.00 |
| C   | 8.21 | 7.41 | 7.15 | 8.00 | 8.00 | 8.00 |

Notes: 1 = Analyzed by Vienna group; 2 = Analyzed by Miami group. CO₃ content by difference. Flink's (1899) type crystal from Narssarssuk was not analyzed.

* By Direct Current Argon Plasma Spectrometer (DCS).
Results for the seven cordylites agree very well, often to minor details. For the least-squares refinement of cordylite from the Kola Peninsula based on the formula (Na, Ca,Ba(Ce, Sr,C1)CO3)O,F because of its SrO content of 5.67 wt% (Table 5): restricting the formula to electronic neutrality resulted in χ = 0.40(1), giving Ce:Sr = 4.0, in good agreement with IREE:Sr = 4.3, as observed in the chemical analysis.

**DESCRIPTION OF THE STRUCTURE**

The structure can be symbolized as a stacking of sheets in (001) as: [Ba] [C2O3] [Ce,C1O3] [Na,F] [Ce,C1O3] [C2O3] [Ba] (depicted in Figs. 1 and 2). The Na and F atoms occupy the same sheet, and this also holds for the C1 and O1 atoms, and the C2 and O2 atoms, respectively. By allowing differences up to 0.69 Å, the Ce atoms belong to the same sheet as the C1 and O1 atoms.

The Ba atoms (point symmetry 3m) are coordinated to twelve O atoms in the form of a distorted hexagonal prism, the Ce atoms (point symmetry 3m) to nine O atoms and one F atom, and the Na atoms (point symmetry 6m2) to six O atoms in the form of a trigonal prism and further to three F atoms at 2.9 Å. Both types of CO3 groups (point symmetry 3m) are slightly aplanar, and their O planes are parallel (001).

The BaO12 polyhedra share six edges among themselves, six edges with CeO3F polyhedra, and six edges with CO3 groups. The CeO3F polyhedra share three edges with BaO12 polyhedra, three edges with NaO6 trigonal prisms, and three edges with CO3 groups, but only corners among themselves. The NaO6 trigonal prisms share six edges with the CeO3F polyhedra; if three F neighbors are included into the coordination, the thus formed NaO6F polyhedra share six O,F faces with the CeO3F polyhedra.

The complete atomic arrangement can be visualized as being built from Ce(CO3)F layers parallel to (001). Two such layers share the F atoms so that Ce(CO3)F double layers are formed that house the Na atoms in cavities. Those double layers are situated at heights c/4 and 3c/4, and they are intercalated by the Ba atoms.

**STEREOCHEMICAL DISCUSSION AND COMPARISON WITH RELATED STRUCTURES**

The interatomic distances (Table 4) agree well with expected values. A notable exception is the unusually large Na-F distance, 2.9 Å, which occurs three times around the Na atoms. The bond distance yields a bond valence of 0.03 v.u., suggesting that the F atoms might not be considered in the first coordination sphere; however, the Na-F vector is not shielded by any O atoms, thus the Na trigonal prism is perhaps better described as a tri-capped trigonal prism. In this context it should be noted that in all seven refinements yielded displacement parameters of U11 for F significantly larger than U11.

In the carbonate groups the deviations of the C atoms
from the plane of its coordinating O atoms is of the usual order of magnitude (cf. Zemann 1981; Effenberger et al. 1983; Chevrier et al. 1992). The orientations of the aplannarity relative to the surroundings follow the rules given by Zemann (1981).

Bond valence sums (Brown 1981) calculated for all atoms in the refined crystal structure of Greenland cordylite-(Ce) by Miami authors yielded Ba = 2.03 v.u., Ce = 3.06 v.u., Ce = 0.95 v.u., C1 = 4.05 v.u., C2 = 3.97 v.u., O1 = 2.05 v.u., and O2 = 2.04 v.u., all in excellent agreement with the formal valence of the ions. The (Na,Ca)O,F site yielded 1.32 v.u. for Na and 2.01 v.u. for Ca, assuming full occupancy by the respective ions.

The results of our seven structure refinements agree very well with those published by Fu et al. (1987) for “baiyuneboite-(Ce).” Our atomic arrangement is also very close to that given by Shen and Mi (1991) for the unnamed mineral (CaO,NO)BaCe4(CO3)5F, although the space group P62c is proferred by those authors. In the structure given by Shen and Mi (1991) the positions of all atoms but one correspond within the limits of accuracy to space group P6/mmc. The exception is their atom 01 for which they give the coordinates 0.455(4), 0.498(4), 0.0656(4). A shift of this atom by 0.19(2) Å could cause that the x and y coordinates to become equal and yield space group P6/mmc for their structure.

Merzier et al. (1993) recognized that the synthetic phase Na1.6La2(CO3)F contains double sheets that are practically identical with those in “baiyuneboite” but intercalated by two Na atoms instead of one Ba. They further noted that huanghoite, BaCe4(CO3)5F (Qian et al. 1982; Mercier and Leblanc 1993a; Yang and Pertlik 1993), contains very similar Ce(CO3)5F layers. However, the layers in huanghoite are not condensed into double sheets but are intercalated by two kinds of Ba atoms. We can also note that in these two structures the carbonate groups are slightly aplanar and that also Na-F = 2.94 Å, which is similar to cordylite. For the more remote relationships to zhonghuacerite, BaCe4(CO3)5F and cebaite, BaCe4(CO3)5F, in both of which the planes of the CO3 groups are essentially parallel to each other, the reader is referred to Mercier and Leblanc (1993b) and Yang et al. (1996).

The most common members of the important group of REE- and Ca-REE-fluorocarbonates, bastnäsite and synchysite (both free of Ba), are also hexagonal or pseudo-hexagonal. From a geometrical point of view they can be described to be built from sheets: e.g., bastnäsite, Ce4(CO3)5F, by a [001] sequence of [CeF] → [CO3] → [CeF] (Ni et al. 1993), and synchysite, CaCe4(CO3)5F, by a [001] sequence of [Ca] → [CO3] → [CeF] → [CO3] → [Ca] (Wang et al. 1994). However the planes of the CO3 groups in bastnäsite or synchysite are perpendicular to (001) and not parallel to each other, and the coordination of the Ce and Ba atoms are different from those of the Ce and Ba atoms in cordylite. Thus the stereochemical relationships of bastnäsite and synchysite to cordylite are remote.

**Problems of Chemical Composition and Nomenclature**

Table 4 and the literature on cordylite (e.g., Yang et al. 1994) show a remarkable variation in the Na/Ca ratio. In material from Narssarssuk, Mont St. Hilaire, and Bayan Obo by (Fu and Su 1987), Na predominates over Ca as “baiyuneboite.” Much of the Bayan Obo material as well as cordylite from Kola peninsula were found to be relatively rich in Ca. The situation is complicated by a SrO content reaching approximately 5.7 wt% in cordylite from the Kola Peninsula with Sr replacing at least in part the Ce atoms. No reliable analyses for H2O in cordylite are available to our knowledge. From the ligature of the F atom (point symmetry 6m2) by two Ce and three Na atoms, extensive replacement of F by OH is improbable if the Na position is fully occupied.

As the replacement of Na+, by Ca, has very little influence on the properties of the crystal, including lattice parameters and X-ray intensities, the determination of the occupancy of the position depends on microprobe analysis. Splitting into two species with end-members NaBaCe4(CO3)5F and (CaO,NO)BaCe4(CO3)5F would in practice cause considerable difficulties and is deemed undesirable.

We agree with Shen and Mi (1992) that the old analyses of cordylite as well as the structure proposed by Ofstedal (1931) need modification. Our investigation of type material redefined the formula as NaBaCe4(CO3)5F and yielded a structure practically identical to that given by Fu et al. (1987) for “baiyuneboite-(Ce).” Cordylites from Narssarssuk, Mont St. Hilaire, Bayan Obo, and Kola peninsula are isostructural, but the Na/Ca ratio and, to a minor extent, the Sr content vary.

As type material of cordylite (Flink 1899; Böggild 1906) is deposited in the mineral collection of the Geologisk Institute, Copenhagen, and as the original description clearly allows definition of the mineral, it seems to us advisable to retain the name cordylite, in any case for members of this mineral with a composition near to the end-member NaBaCe4(CO3)5F and to abandon the name “baiyuneboite-(Ce).”

**ACKNOWLEDGMENTS**

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